

PATENT SPECIFICATION

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DRAWINGS ATTACHED



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(54) IMPROVEMENTS IN AND RELATING TO SHEET MATERIAL

- (71) We, RANSBURG ELECTRO-COATING CORP., a corporation organised and existing under the laws of the State of Indiana, United States of America of 3939 West 56th Street, Indianapolis, Indiana, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to the manufacture of cellulosic sheet material such as paper and paperboard in which the properties are altered by the application of dry particulate water-sensitive material.
- According to the invention there is provided a method for manufacturing fibrous, absorbent, cellulosic sheet material, including the steps of forming a water-wet web of the material, charging electrostatically dry particles of water-sensitive bonding material, as hereinafter defined, whereby to cause said particles to repel one another and to be deposited on said water-wet web as substantially separated particles, and dewatering said web after said particles have been so deposited. The invention also comprises the products of the method. We use the term "water-sensitive bonding material" herein to mean natural resins such as rosin, hydrogenated rosin and partial esters of rosin; proteins, such as zein, which are soluble either in water or in dilute alkali; ester gums; natural gums such as gum arabic, agar-agar, Irish moss; synthetic resins such as polyvinyl alcohol and acrylic ester/carboxylic acid copolymers; and carboxy-methyl-cellulose. The use of starch as a binding material is excluded from the scope of the present application as it is within the scope of our co-pending application No. 888/68 (Serial No. 1,221,951).
- In a form of the invention described hereinafter a water-wet sheet of fibrous, cellulosic material is advanced past a particle-deposition zone and electrostatically charged particles of dry water-sensitive bonding material are supplied to this zone, these charged particles repelling one another to become uniformly distributed while they are attracted to the wet paper web which is effectively earthed. These particles are in an electrostatic field which extends to the web and are deposited as individual separated particles and they tend to remain associated with the surface fibres so that the surface characteristics of the paper or paper-board being treated can be preferentially modified. The wet sheet with the bonding material particles deposited on the surface thereof is then dried, preferably using heat to facilitate the reaction with water and the deposited particles become adhesively related to the surface fibres to help to bind them to the body of the paper and to modify other surface characteristics.
- Some examples of the invention involve the utilization of water-sensitive bonding materials so that these may interact with the water of the wet paper during its formation either in the presence or absence of the heat normally used for the drying of the paper in order that the applied bonding material may become intimately associated with the fibres of the paper. However, when particulate materials are deposited upon paper containing more than 25% by weight of water, there is a strong tendency for these particles to penetrate the body of the paper and become uniformly distributed throughout the same. Indeed, in the presence of larger proportions of water, unless there is some attraction between the paper fibres and the particles as may occur when cationic bonding materials are employed in the paper furnish, there is a strong tendency for much of the particulate material to penetrate entirely through the paper web and be lost with the white water.
- The invention is applicable to water-sensitive bonding materials of diverse type including natural resins and synthetic resins.

These substances may differ in their chemical nature, and can also differ in the extent and character of their sensitivity to water.

To illustrate the diverse types of water-sensitive binding material which may be used, resin is illustrative of natural resins which have considerable affinity for water and which can function in the invention as a size with the rosin particles remaining in the vicinity of the surface of the paper until the combination of drying temperature and contact time causes the rosin to become dispersed in the water. By selecting a slowly soluble rosin sizing material, the dispersing of the rosin particle in the water can be delayed to occur when the moisture content of the paper has been greatly reduced so that the bulk of the dispersed rosin remains near the surface. The rosin is desirably used in the form of a soap with a non-volatile base such as sodium hydroxide. Partial esters of rosin with an alcohol such as ethyl alcohol, butyl alcohol or 2-ethyl-hexyl alcohol can also be used, again preferably as a soap.

The application of rosin is usually performed together with the utilisation of alum in the furnish, the alum serving to convert the electronegative cellulose fibres into electropositive fibres which have an affinity for rosin which is usually electronegative. It is preferred to incorporate alum in the furnish and then to use rosin particles which retain a negative charge when they are earthed. In this connection, it is preferred to employ rosin particles having a surface portion of increased conductivity and to use a power pack connected to supply a positive voltage so that a negative charge is retained after the charged particle has been earthed. The surface portion of increased conductivity is easily provided by soap formation at the surface with a base or by the application of a proportion of alkali metal compound which leaves excess alkali at the surface such as by treatment with a concentrated aqueous solution of sodium carbonate. This provides more rapid solubility in the aqueous medium of the paper web as well as forming the conductive surface portions which tend to create particle structures which retain opposite charges after earthing.

Other natural bonding materials which may be utilized are zein and other proteins which are soluble either in water or in dilute alkali. Similarly, ester gums can be used as well as the natural gums such as gum arabic, agar-agar and Irish moss. Many of the natural gums are acidic and their affinity for water can be enhanced by soap formation. Moreover, the extent of solubility can be controlled by the extent of soap formation. Gelatin is also a useful bonding material.

Referring to the synthetic materials, poly-

vinyl alcohol of low acetate content is particularly desirable as a bonding material which swells with water, but does not become significantly dispersed. In the presence of moisture and heat, polyvinyl alcohol becomes swollen with water and is adhesive to provide a desirable binding effect for the surface fibres. Polyvinyl alcohol is produced by the hydrolysis of polyvinyl acetate. When substantially complete hydrolysis is effected, e.g. approximately 98.5%, then a sizing material having good fibre-binding characteristics is provided and the adhesive product provided is reasonably water-resistant. These materials in powder form are useful to bind surface fibres with minimal reduction in the absorbency of the paper which is modified. At a lower extent of hydrolysis, e.g. 86—89%, the product is more water-sensitive and forms a size which disperses in the surface regions of the paper to combine fibre-adhesion with a greater increase in resistance to water-absorption.

Synthetic resins having extensive solubility in water are illustrated by polyvinyl acetate hydrolysed to an extent of from 60—85% and also by acrylic ester carboxylic acid copolymers such as a solution copolymer obtained by copolymerising 80 parts ethyl acrylate with 20 parts of acrylic or methacrylic acid. These acrylic ester/carboxylic acid copolymers can be placed in salt form (soaps) by reaction with a non-volatile base, such as sodium hydroxide, and an aqueous solution thereof dried to provide the copolymers in salt or soap form which then dissolve rapidly in water.

It is also possible to utilise bonding materials which have little affinity for water at ordinary temperatures but which are extensively soluble in water at the more elevated temperatures encountered in the ordinary drying of paper utilizing steam-heated dryer rolls. In this connection, reference is made to carboxy-methyl-cellulose which can be associated with the surface paper fibres in accordance with the invention to retain its particulate form until late in the paper-making process when the more elevated drying temperatures are encountered at which time the particles can dissolve to modify the water-absorption properties substantially only in the vicinity of the surface of the paper. Polyvinyl alcohol and gelatin also become more soluble as the temperature is raised.

While different bonding materials may be preferred in order better to achieve the different objects which are embraced within the process of the invention or to accommodate the different conditions of paper manufacture which are employed, such as machine speed, point of application, dryer-roll temperature and the like, it will be understood that the various materials noted previously

can be used alone or in mixtures. The use of mixtures is illustrated by mixtures of polyvinyl alcohol of different water dispersibility to obtain intermediate properties.

5 Broadly, the particle size of the bonding material can vary within the range of from 40—300 mesh, and even smaller particles may be desirably used. Preferably, the particle size is 80 mesh or smaller. Indeed, particles having an average diameter of one-fifth to one-tenth the average width of the paper fibres may be easily handled in the invention.

10 Features and advantages of this invention will become apparent from the following description of embodiments thereof, taken in conjunction with the drawings, in which:

15 Figure 1 is a perspective view illustrating a paper-making machine including means for the deposition of electrostatically charged particles on the paper web according to an example of the invention, and

20 Fig. 2 is a partial diagrammatic view illustrating some alternative methods for the electrostatic application of the bonding material particles to the paper.

25 Referring first particularly to Fig. 1, the numeral 10 generically identifies a Fourdrinier machine comprising a head box 11, a slice 12, a breast roll 13, table rolls 14, and a couch 15 around which the wire 16 travels. The conventional dandy roll may be present if desired, but this roll is not shown. The conventional suction boxes are identified by the numeral 17. When the freshly formed wet paper web leaves the wire 16, it is moved to the presses, the press rolls being identified by the numeral 18 and the felts which transport the paper being identified by the numerals 19, 20 and 21.

30 The paper P as originally deposited from the head box 11 onto the wire in the vicinity of the breast roll 13 is mostly water and the water content is reduced progressively by drainage and then by suction to a level of roughly 80% in the vicinity of the couch roll 15. After the paper leaves the couch roll, it is passed to a press section where the press rolls 18 co-act further to express water from the paper web still further to reduce the water content of the paper and further to increase the internal strength of the sheet. Lastly, the partially dewatered web is passed to the dryers D which reduce the sheet moisture content further to the level desired in the finished product.

35 In Fig. 1 electrostatically charged bonding material particles are deposited upon the upper or felt side of the paper P before the paper web is advanced through the first pair of press rolls 18. As can be seen, the bonding material particles are supplied as indicated by the arrow 22 through a header 23 and then, with tubes 24 to distributing heads 25 which are positioned above the surface of

the paper P. A metered amount of finely divided bonding material is blown in, scattered by the distributing heads 25 and these particles are electrostatically charged so as to form a uniform cloud of bonding material particles within the chamber 26 which are propelled into association with the paper P by virtue of their electrostatic charge as has been described.

70 The powder-application assembly may be positioned at any of various points along the travel of the Fourdrinier wire. It may be positioned between two or in place of one of the sets of press rolls or it may be located between the last set of press rolls and the dryer section. Similarly, it may be inverted and used to electrostatically apply the bonding material particles to the undersurface or wire side of the paper as indicated by the arrow 32. The invention is not limited to operation on a Fourdrinier machine but is equally advantageous on cylinder or other machines.

75 There is illustrated in Fig. 2 the application of bonding material particles to both sides of the wet web P as it is moved through a vertical path as may occur as it travels between adjacent pairs of press rolls 18. For sake of illustration, on one side of the vertically moving wet web is a fluidized bed 33 of electrostatically charged bonding material particles, numeral 34 indicating a cloud of bonding material particles being electrostatically transported out of the fluidized bed 33 and into engagement with the wire side of the wet paper. Another structure for applying the bonding material particles electrostatically to the vertically moving paper web is shown for dusting the felt side of the paper web. Here the structure is diagrammatically indicated in the form of an inclined platform 35 which is agitated as indicated by the double-ended arrow 36 so that a metered amount of particles is uniformly dropped into the vicinity of the paper web from the lower end of the platform 35 where the electrostatic charge on the particles forms a cloud 37 in which the bonding material particles are electrostatically transported into engagement with the wet paper.

80 As illustrated, the electrostatic application of bonding material particles or granules in metered amounts from a position above or below the wet web can be achieved in various ways, the utilization of an inclined plate which is agitated to feed the particles and charged to charge the particles is feasible, such structures being shown in United States patent 2,748,018. The use of guns to project or spray metered proportions of electrostatically charged particles is preferred. These structures can also be utilized to apply the particles to the paper as it moves through a vertical traverse thereof, in which case the

supply of uncharged particles might well fail to deposit anything on the paper. When the charge is applied, the electrostatic transporting forces again control the flow rate of material as well as the deposit of the particles on the paper. In the preferred situation, the particles which are projected toward the paper or dropped upon it are charged, but uncharged particles can also be used and charged on the way to the paper, which can be accomplished by passing them through an electrostatic field.

The bonding material particles can be applied on one or both sides of the paper, but preferably to the upper or felt side of the paper web, it being observed that the wire side of the paper web is normally much stronger than the felt side so that it is sometimes sufficient to modify and strengthen only the felt side of the paper in order to provide a satisfactory product. On the other hand, and in the production of finer grades of paper, it is frequently desirable to apply the bonding material particles to both sides of the paper web and this can be done.

The moisture content of the paper web at the point of deposition of the bonding material particles is important to the operation, but so is the moisture-temperature balance in the dryers as this moisture is removed. More particularly, a moisture content of from 25% to 95% by weight of water or more may be used, but it is preferred that the web moisture content at the time of bonding material deposition should be at least 45% by weight, preferably above 60% by weight. This is because at moisture contents of 45% or more, there is a greater opportunity of the bonding material particles which are deposited to imbibe moisture to provide the characteristics which are desired, but this will vary with the bonding material selected, the temperatures used for drying and the purpose contemplated. Thus, the point of bonding material application may be varied to help to control the extent of bonding material dispersion which is achieved.

In the manner of electrostatic deposition described for depositing dry bonding material particles on the surface of a paper web, the deposition is not noticeably affected by the turbulence of the air near the wire. The operation is free from dust and substantially all of the bonding material is deposited on the web. Additionally the charged particles in transit between the distributing equipment and the paper web repel each other so that there is no tendency for them to form agglomerates or clumps and the resulting cloud of material is exceptionally uniform and deposits on the sheet surface in a very uniform manner.

As the wet paper web passes through the particle-deposition zone it is exposed there-

in to an electrostatic field from the charged distributing heads. These heads are charged to establish a field having an average potential gradient of at least five and preferably from five to ten kilovolts per inch of distance extending between the distributing heads and the surface of the effectively earthed web. It should be noted that the paper web itself is subjected to the electrostatic field which may induce conditions of field concentration in the vicinity of the protruding surface fibres or the field may induce other related effect on the wet paper web which can contribute to the observed phenomenon in which the bonding material particles remain at the surface in association with the paper fibres instead of grossly penetrating the web as would be expected from the high moisture content of the paper web at the point of bonding material deposition and from the small size of the particles which may be deposited.

The electrostatically charged bonding material particles are attracted to the wet paper surface and this attraction is able effectively to overcome the turbulence created by the air which moves along with the rapidly advancing web. The deposited particles remain at the surface of the paper and it is thought that there is a selective deposition of particles on those fibres protruding above the surface of the sheet. These are the fibres which have the greatest susceptibility to picking, that is removal by the inked surface, during the printing operation, from the remainder of the sheet. It is believed that this phenomenon of selective deposition on such portions of the web contributes to the unexpected, markedly improved sheet properties resulting from the use of very small quantities of electrostatically deposited bonding material.

In the process described, the amount of bonding material applied can be varied considerably while still achieving some benefits. Preferred results are obtained by applying a small proportion of bonding material, such as .02 to .3 lbs. of bonding material per 1,000 sq.ft. of treated surface. The method of this invention can be used to apply from .02 to 2.0 lbs. of bonding material per 1,000 sq. ft. of surface.

As will be understood, the application of bonding material particles in accordance with the invention may be accompanied by the simultaneous application of other particulate materials which can be blended with the bonding material particles and applied together therewith. These other particulate materials are illustrated by pigments and fillers such as clay and like mineral fillers.

It has been found that the association of the deposited bonding material particles with the surface fibres of the wet paper web is enhanced, by utilizing particles of which a

surface region is more conductive than the core. The use of such bonding material particles is preferred since such particles tend to retain a charge after the initially charged particles have been earthed. Frequently, the retained charge is opposite in sign to the charge initially imposed, e.g. the charge initially imposed on the bonding material particles is desirably negative and, after earthing, a positive charge is retained. Since the cellulosic paper fibres are frequently electronegative, the preferential association of positively charged solid particles by electronegative paper fibres at the surface of the paper will be evident. Of course, when the paper fibres are modified with alum to make them electropositive, then a positive charge can be applied to the bonding material particles.

The provision of particles having a conductive surface portion and a less conductive core portion can be provided in diverse ways. To illustrate, many of the water-sensitive bonding materials which may be used in the invention are acrylic ester/carboxylic acid copolymers in which the capacity for association with water is by means of salt formation with a base. In order that the aqueous phase of the paper furnish may be utilized without pH adjustment, the copolymer is reacted with a non-volatile base such as sodium or potassium hydroxide or with a slowly volatile base, such as a higher-molecular-weight amine like dodecylamine, in order to form a soap which can react directly with the water. In this embodiment of the invention, the soap is formed at the surface of the copolymer particle by thoroughly mixing together the copolymer particles with a small amount of water containing the base and then evaporating the water to provide particles which are more conductive at the surface and which tend to retain after earthing a charge opposite to that which is applied.

To illustrate the foregoing with particles which do not become disrupted upon association with water, a solution copolymer containing 95% units derived from ethyl acrylate and 5% units derived from acrylic acid in the form of spray-dried particles is mixed with 50% by weight of 2% aqueous sodium hydroxide and air is blown through the mixture to dry the same leaving behind copolymer particles having a conductive surface sensitive to water.

Rosin, hydrogenated rosin and partial esters of rosin may be treated in the manner noted above and deposited on the wet paper, alum preferably having been preassociated with the paper fibres in the furnish. In this way, the aluminum rosinate is formed at the upper surface of the paper web and the normal tendency of rosin sizes to clog the felts is substantially eliminated. This is true

even when the rosin particles are applied to both surfaces of the web since the rosin particles have a strong tendency to remain in contact with the surface fibres and the tendency of dispersed fragments of aluminum rosinate to contaminate the surrounding felts is reduced by the reduced contact between the water and the rosin particles and the electrostatic adhesion which can be developed between the paper fibres and the rosin particles.

The invention is illustrated in the following Examples.

EXAMPLE 1

An experimental papermaking machine (generally similar to the one illustrated in Figure 1) and including a bonding material application assembly utilizing equipment as indicated by numerals 22, 23, 24, 25 and 26 shown in Figure 1 was used to transport and electrostatically deposit a finely divided polyvinyl alcohol on the wet paper web. A single electrostatic distributing head 25 was used at about 10 to 12" above the web, but in commerce wider webs would be produced and more distributing heads would be used as shown in the drawing to apply the starch across the full width of such wider webs. The furnish used approximated a conventional newsprint (70% groundwood—30% sulphite) and the final sheet weighed 32 lbs. per ream (24"×36"—500 sheets) (3,000 sq. ft.).

The papermaking machine was operated at a speed of 75 feet per minute and polyvinyl alcohol particles (polyvinyl acetate hydrolyzed to 98.5%) were applied to the felt side of the paper utilizing an electrical potential of 65—75 kilovolts on the heads, said potential being applied by a negative power pack. The polyvinyl alcohol particles were screened to remove particles larger than 80 mesh. The particle-application equipment was located so that the polyvinyl alcohol was applied to the upper surface of the sheet at a location between the last press rolls and the first dryer roll, the sheet moisture content in this region being about 65%. Following application of the polyvinyl alcohol, the sheet was continuously dried using dryer rolls heated with 30 p.s.i.g. steam and the dried sheet was calendered. The rate of application of the polyvinyl alcohol was such that the amount deposited was equivalent to 1% of the weight of the paper fiber, about .1 lbs per 1000 sq. ft. surface. The finished sheets showed increased pick-resistance and surface strength as compared to the same sheet without the polyvinyl alcohol, but the capacity to absorb oily links was substantially unchanged. The use of 2% and 3% polyvinyl alcohol led to further improvement in pick-resistance and surface strength.

Essentially the same results were obtained

utilizing the commercial polyvinyl alcohols sold in the U.S.A. by Airco Chemical, under the trade identifications VINOL 325, VINOL 350, and VINOL 125.

EXAMPLE 2

5 The procedure of Example 1 was repeated while applying the polyvinyl alcohol powder at the 1% level or about .1 lbs. per 1000
10 sq. ft. For different portions of this run, the electrostatic application equipment was positioned successively at (1) a position between the last press roll and the first dryer roll where the sheet moisture was about 65%,
15 (2) immediately ahead of the couch roll as illustrated in Figure 1 where the sheet contained about 83% moisture, (3) further back over the paper machine wire where the sheet moisture content is approximately 94%. In
20 each case, the machine operation was satisfactory and the products were comparable regardless of the location of the application equipment.

EXAMPLE 3

25 The procedure of Example 1 was again repeated but this time the polyvinyl alcohol was electrostatically deposited on the top of the sheet by a unit positioned over the sheet between the last press roll and the first dryer roll, and also on the bottom of
30 the sheet by a unit positioned under the sheet at this same location. No operational problems were encountered and improvement in surface pick-resistance tests and strength was observed on both the top and
35 bottom of the sheets.

EXAMPLE 4

40 Examples 1—3 were repeated using finely powdered carboxy-methyl-cellulose as the bonding material in place of the polyvinyl alcohol (screened to remove particles over 80 mesh). Comparable results were obtained.

EXAMPLE 5

45 Examples 1—3 were repeated using finely divided copolymer particles (a spray-dried solution copolymer containing 95 weight per cent units derived from ethyl acrylate and 5 weight per cent units derived from methacrylic acid, reacted with a stoichiometric proportion of sodium hydroxide as the bonding material. The particles passed
50 through an 80 mesh screen before use. The copolymer particles swelled and became adhesive to bind the surface fibres of the paper. Refrigeration was used in some examples to minimize sticking of the copolymer particles prior to use. Overcoating the copolymer
55 particles by mixing them with 15% by weight of a 5% sodium carbonate solution increased the retention of the particles on the surface of the paper.
60

EXAMPLE 6

Examples 1—3 were repeated utilizing a furnish of 50% groundwood and 50% sulphite to deposit a final sheet weighing 28
65 lbs. per ream in order to form an appropriate base for a publication-grade paper. Alum was incorporated in the furnish, but rosin was omitted. Operating the paper-making machine as in Example 1, rosin particles were used as the bonding material (screened to remove particles larger than 80
70 mesh) and were applied as in Example 1 in place of the polyvinyl alcohol, the rosin being in the form of a soap having an acid number of from 0—7 and containing 1.4%
75 free alkali expressed as sodium bicarbonate. The final product was significantly upgraded by the rosin which reduced the water absorption and increased the ink-holdout capacity
80 of the paper. The rosin appeared to perform more efficiently than was the case when the same proportion of rosin was incorporated in the furnish.

Washing the rosin with 15% by weight of a 5% sodium carbonate solution was helpful
85 in achieving improved solubility and confinement of the rosin size to the surface region of the paper. This latter effect was also enhanced by utilizing a power pack connected
90 to supply a positive voltage instead of one connected to supply the more usual negative voltage.

Essentially the same results were obtained utilizing commercial rosins sold by Hercules
95 Powder Co. under the following trade designations: Dry Pexol (Registered Trade Mark), Dry X Rosin Size, Dry XXX Rosin Size and Dry Size 248.

EXAMPLE 7

100 Examples 1—3 were repeated utilizing a bleached Kraft furnish depositing a final sheet weighing 36 lbs. per ream and as the bonding material, a polyvinyl alcohol made from polyvinyl acetate hydrolysed to an extent of approximately 87%. The use of polyvinyl alcohol having a lower extent of hydrolysis resulted in a greater dispersion of the
105 polyvinyl alcohol in the surface regions of the paper to increase the resistance to water absorption and provided an excellent base for subsequent coating and calendering in the production of paper of superior print quality.
110

EXAMPLE 8

115 Example 7 was repeated utilizing a solution copolymer having 80% units derived from ethyl acrylate and 20% units derived from methacrylic acid, in the form of a spray-dried product which was mixed with 30 parts
120 by weight of a 5% sodium carbonate solution and then dried to provide rapid surface solubility and the production of a paper in which the applied copolymer was concen-

trated in both dispersed and particulate form near the surface to which it was applied.

Attention is directed to our co-pending Application No. 888/68 (Serial No. 1,221,951) in which there is claimed apparatus for manufacturing paper comprising means to support a web of paper pulp, means to supply paper pulp to form a web of the pulp on the support, and means for depositing on the web a material in the form of dry particles, said depositing means comprising gas-operated means for producing a cloud of the particles and means for charging the particles electrostatically.

15 WHAT WE CLAIM IS:—

1. A method for manufacturing fibrous, absorbent, cellulosic sheet material, including the steps of forming a water-wet web of the material, charging electrostatically dry particles of a water-sensitive bonding material, as hereinbefore defined, whereby to cause said particles to repel one another and to be deposited on said water-wet web as substantially separated particles, and de-watering said web after said particles have been so deposited.

2. A method according to claim 1 in which said particles are formed to include surface portions of increased conductivity surrounding a more resistive or insulating core. 30

3. A method according to any of the preceding claims in which said water-wet web contains at least 25% by weight of water.

4. A method according to any of the preceding claims in which said water-wet web contains at least 45% by weight of water. 35

5. A method according to any of the preceding claims in which said charged particles are deposited by an electrostatic field having an average potential gradient of at least 5 kilovolts per inch. 40

6. A method for the manufacture of fibrous, absorbent, cellulosic sheet material substantially as herein described. 45

7. A paper when produced by a method according to any of the preceding claims.

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1221952 COMPLETE SPECIFICATION.

1 SHEET

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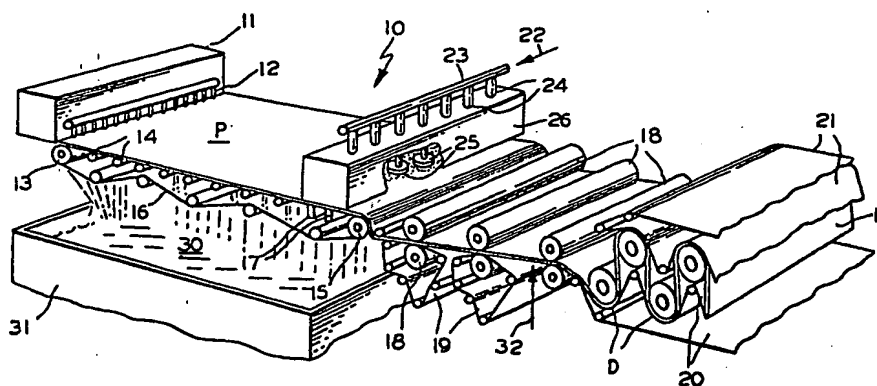


FIG.1

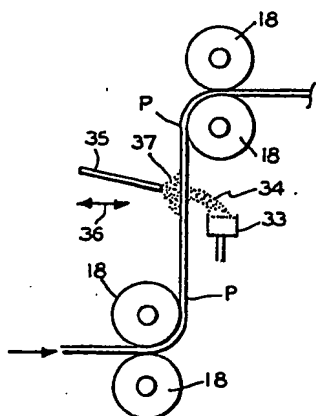


FIG. 2